Synthesis and Characterization of Bi-based Electrodes for Supercapacitor

Synopsis in Candidature for the Degree of

Doctor of Philosophy in Physics

Submitted by

Mr. Hanmant Kadam

Under the guidance of

Dr. Shyam K. Gore

Dnyanopasak College Jintur

Submitted to

स्वामी रामानंद तीर्थ मराठवाडा विद्यापीठ, नांदेड.

1. Introduction

Facing a severe global energy crisis and environmental pollution, as well as the ever-growing needs for green energy conversion devices, portable electronic devices and hybrid electric vehicles, considerable efforts have been made in exploring advanced performance and eco-friendly energy storage devices in the past several decades [1-5]. Electrochemical capacitors, which are also called supercapacitors (SCs), have attracted tremendous interest owing to their outstanding merits, such as high energy and power densities, fast discharge/charge process and long cycle life [6-8]. The shortage of drinking water, electricity, fuel, and air is increasing, and this shortage is harmful for both the living creatures and environment [1,2]. It is crucial to use renewable energy sources for improving human health and environment; therefore, various possibilities for renewable energy solutions have been investigated. The efficient design of batteries, fuel cells, and SCs has become crucial for fulfilling the basic needs in both developed and under-developed countries. Supercapacitors with zero-dimensional (0D) to three-dimensional (3D) RuO_2, MnO_2, $Co3O_4$, NiO, SnO_2, In_2O_3, Bi_2O_3, V_2O_5, Fe_3O_4, $BiFeO_3$, and $NiFe_2O_3$ nanoelectrodes synthesized using various chemical and physical deposition methods have been investigated for commercialization [3-5]. Among these electrode materials, bismuth (Bi)-based compounds, such as oxides, chalcogenides, and halides, can be used for a broad spectrum of applications including solar cells, gas sensors, ferroelectricity, supercapacitors, and batteries. The oxides and sulfides of bismuth (Bi), which is commonly found within the Earth's crust, have been found to be useful for various applications [6,7]. Bi is usually pink in color, and has a lower thermal conductivity and less toxicity than those of heavy metals, such as Hg, Cd, Sn or Pb. Majority of the studies based on Bi-based compounds have majorly focused on β-Bi_2O_3, δ-Bi_2O_3, ε-Bi_2O_3, α-Bi_2O_3, and γ-Bi_2O_3 polymorphic phases. In a polymorph, two Bi atoms are coupled with three O atoms via different co-ordinations as five- and six-fold symmetry [8]. Hence, bi-based electrodes will be excellent active electrodes for energy storage application in the near future.

2. Literature review

The use of Bi-based electrode materials prepared by various chemical processes with different morphologies and structures have been envisaged in energy applications. The Bismuth based active electrode in energy storage is substantially increasing due to its large surface area and excellent conductivity [9]. Bismuth oxide (Bi_2O_3) has drawn considerable attention because of its large energy band gap (2.8 eV) [10], good oxygen-ion conductivity, high dielectric permittivity, nontoxicity, and biocompatibility. In addition, Bi_2O_3 has a long durability cyclic performance, depending on its polymorphic form. Bi_2O_3 can exist in five polymorphs, where low-temperature α-Bi_2O_3 (monoclinic) and high-temperature δ-Bi_2O_3 (cubic) are highly stable [11]. Additionally, the layered structure of Bi_2O_3 promotes the employment of Bi_2O_3 as an interesting host for energy storage [12]. The main drawback of bi -electrode is the poor conductivity and chemical irreversibility have impeded their applications in energy storage devices; however, this can be sorted out by adjusting different parameters, such as tuning the surface morphology, controlling crystal structure, doping ad-atom to enhance conductivity, and maintaining high porosity and active sites. Coupling with other metal oxide materials and/or doping with elements of several redox reactions or higher conductivities are few methods for enhancing the energy storage performance of Bi-based electrode materials.

Notwithstanding this, Bi-based electrodes have not been studied in depth for their electrochemical behavior, and it is still highly desirable and challenging to develop Bi-based electrode with good performance. 3D hierarchical Bi-based nanostructures are rarely reported for supercapacitor device fabrication, although they are highly desirable for achieving enhanced electron transport, improved ionic diffusion, and excellent rate capability [13-15]. Therefore, it is imperative to develop systematic and rational techniques to construct bi-based nanostructured electrode for supercapacitor. The proposed work focused on the synthesis of Bi-based electrode for supercapacitor fabrication using chemical method.

3. Aim

The focus of present work is to develop bi-based asymmetric and asymmetric supercapacitors based on composite nanostructures. These asymmetric supercapacitors

consist of a battery-type Faradaic electrode (as the energy source) and a capacitor-type electrode (as the power source), simultaneously offering the advantages of both supercapacitors (rate, cycle life) and advanced batteries (energy density). Therefore, asymmetric supercapacitors can make full use of the different potential windows of the two electrodes to provide a maximum operation voltage in the cell system, accordingly resulting in a greatly enhanced specific capacitance and significantly improved energy density.

4. Objective

The main objective of the proposed synopsis is to develop and synthesis novel bi-based hybrid electrodes for super capacitors performance. The materials include metal oxides, composites of metal oxide and graphene oxide.

- Synthesis of 3D structured bi-based electrodes.
- Structural and morphological properties of the prepared bi-based nanostructured electrodes will be studied using various characterization techniques such as X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), high resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, etc.
- Obtained high specific capacitance, cyclic life, excellent rate capability.
- Fabrications of symmetric and asymmetric supercapacitor.
- Work will have published in reputed journals.

5. Synthesis method

There are many chemical methods are used for synthesis of bi-based and composite electrodes such as hydrothermal deposition (HD), chemical bath deposition (CBD), electrodeposition (E-D), successive ionic layer adsorption and reaction (SILAR), sol-gel, and spray pyrolysis deposition (SPD), have frequently been used to obtain myriads of Bi-based nanostructures in both film and powder form. These vacuum-free chemical methods do not require complex and expensive instrumentations. Few methods are as follows;

5.1 CBD (Chemical bath deposition)

The metal oxide/bi-based electrode prepared by adjusting CBD preparative parameters, such as deposition temperature, time, pH, complexing agent etc. The metal oxide films were deposited from the solution containing precursor by using different complexing agent.

5.2 SILAR (successive ionic layer adsorption and reaction)

SILAR method is economically, highly feasible for large area deposition and wastage of chemicals can be avoided. For the deposition of material thin film, a well-cleaned glass substrate was immersed in the cationic precursor solution, causing cations to be adsorbed on the surface of the glass substrate. This substrate was immersed in an ample amount of double distilled water to prevent homogenous precipitation. The substrate was then immersed in the anionic precursor solution. Anions reacted with the adsorbed cations on the glass substrate. The substrate was then immersed in double-distilled water.

5.3 Hydrothermal

Many types of nanomaterial/metal oxide have been successfully synthesized by using hydrothermal. There are significant advantages of hydrothermal synthesis method over others. Hydrothermal synthesis can generate nanomaterial which are not stable at elevated temperatures. Nanomaterial with high vapor pressures can be produced by the hydrothermal method with minimum loss of materials. The compositions of nanomaterial to be synthesized can be well controlled in hydrothermal synthesis through liquid phase or multiphase chemical reactions.

Among these methods, optimized method will be used for synthesis of bi-based electrodes for supercapacitor application.

6. Experimental section

Synthesized Bi-based electrodes will be characterized by using different analytical tools and techniques such as X-ray diffraction (XRD), Raman spectroscopy, Fourier Transform Infrared Spectroscopy, Field Emission Scanning Electron Microscopy (FE-SEM), High Resolution Transmission Electron Microscopy (HR-TEM) X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS), etc.

Electrochemical workstation will be used to study the electrochemical properties and device fabrication. Finally, carried work will be submitted to the university for the award of Ph.D. in the form of thesis.

7. Outcomes;

- ✔ Supercapacitor device will be fabricated using bi-based electrodes.
- ✔ Result will be published in the reputed journals.

8. Reference

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Signature	Signature
Research Student	Research Supervisor/Guide/Co-guide